U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
33764R003

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)
09/787667

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/BR99/00079	21 September 1999	21 September 1998 19 April 1999

TITLE OF INVENTION
RADIATION SENSITIVE COATING COMPOSITION USEFUL FOR LITHOGRAPHIC PRINTING PLATES AND THE LIKE

APPLICANT(S) FOR DO/EO/US --- Andre Luiz ARIAS, et al..

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ■ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.

2. □ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C 371.

3. ■ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).

4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. ■ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
a.■ is transmitted herewith (required only if not transmitted by the International Bureau)b □ has been transmitted by the International Bureau (see Form 308) c. □ is not required, as the application was filed in the United States Receiving Office (RO/US).

6. □ A translation of the International Application into English (35 U S.C. 371(c)(2))

7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S C. 371(c)(3))
a.□ are transmitted herewith (required only if not transmitted by the International Bureau)
b. □ have been transmitted by the International Bureau.
c. □ have not been made; however, the time limit for making such amendments has NOT expired.
d. ■ have not been made and will not be made.

8. □ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. □ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. □ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ■ An Information Disclosure Statement under 37 CFR 1.97 and 1.98. (w/ copy of PTO-1449 and each reference cited therein and Int'l Search Rept)

12. □ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ■ A FIRST preliminary amendment.
□ A SECOND or SUBSEQUENT preliminary amendment.

14. □ A substitute specification

15. □ A change of power of attorney and/or address letter.

16. ■ Other items or information:

a) PCT Request (Form PCT/RO/101)
b) Notification of Transmittal of the International Search Report or the Declaration (PCT/ISA/220),
c) International Search Report (PCT/ISA/210);
d) Notification of Transmittal of the International Preliminary Examination Report (PCT/IPEA/416);
e) International Preliminary Examination Report (PCT/IPEA/409) **including the amended claim set to be prosecuted;**
f) PCT Publ. WO 00/17711 with Search Report
g) PCT Written Opinion (Form PCT/IPEA/408)
h)Applicants' Reply to Written Opinion dated September 18, 2000
i) PCT Chapter II Demand (PCT/IPEA/401)

U S DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER 33764R003

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/787667

17. ■ The following fees are submitted:	CALCULATION	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO . . . . . $860.00 International preliminary examination fee paid to USPTO (37 CFR 1 482) . . . . . $670.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2) . . . . . $760.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . $970.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $96.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than □ 20 □ 30 months from the earliest claimed priority date (37 CFR 1.495(e)).	$ -	

Claims	Number Filed	Number Extra	Rate		
Total Claims	22 - 20 =	2	x $18.00	$ 36.00	
Independent Claims	1 - 3 =	-	x $80.00	$ -	
Multiple dependent claim(s) (if applicable)			+ $260.00	-	
TOTAL OF ABOVE CALCULATIONS =				$ 896.00	
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$ 0 00	
SUBTOTAL =				$ 896.00	
Processing fee of $130.00 for furnishing the English translation later than □ 20 □ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ -	
TOTAL NATIONAL FEE =				$ 896 00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3 31). $40.00 per property. +				$ 0 00	
TOTAL FEES ENCLOSED =				$ 896.00	
				Amount to be refunded	$
				charged	$

a. ■ A check in the amount of $ 896.00 to cover the above fees is enclosed.
b. □ Please charge my Deposit Account No. 02-4300 in the amount of $____ to cover the above fees. A duplicate copy of this sheet is enclosed.
c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required with respect to any deficiency in the above noted "Basic National Fee", or credit any overpayment to Deposit Account No. 02-4300 .

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

SMITH, GAMBRELL & RUSSELL, LLP
1850 M Street, NW - Suite 800
Washington, DC 20036

Tel: (202) 659-2811
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SIGNATURE

Dennis C. Rodgers - 32,936
NAME REGISTRATION NO.

Date: March 21, 2001

Atty. Docket No.
33764R003

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Andre Luiz Arias, et al.

US Serial No.: 09/787,667 Group Art Unit: To Be Assigned

Filed: March 21, 2001 Examiner: To Be Assigned

For: RADIATION SENSITIVE COATING COMPOSITION USEFUL FOR LITHOGRAPHIC PRINTING PLATES AND THE LIKE

SUPPLEMENTAL PRLIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Further to the Preliminary Amendment of March 21, 2001, please find enclosed a clean version and marked version of some further claim amendments.

REMARKS

The accompanying amendments are intended to correct the dependency indication made in the Preliminary Amendment filed March 21, 2001, such that process claims 20-22 depend from the more basic process Claim 17.

If any fees are due in connection with the filing of this Amendment or any papers that accompany it, such as fees under 37 C.F.R. §§ 1.16 or 1.17, please charge the fees to our Deposit Account No. 02-4300.

Respectfully submitted,

SMITH, GAMBRELL & RUSSELL, LLP

By: _____

Dennis C. Rodgers, Reg. No. 32,936
1850 M Street, N.W., Suite 800
Washington, D.C. 20036
Telephone: (202) 659-2811
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June 11, 2001

Marked Up Version of Claim Amendments

20. Process according to claim 17 [1], wherein the composition is dissolved in an appropriate solvent system.

21. Process according to claim 17 [1], wherein the composition is applied to provide a coating having dry weight in the range from 1.5 g/m2 to 3.0 g/m2.

22. Process according to claim 17 [1], wherein the composition is applied to provide a coating on a textured and anodized aluminum substrate or on a polyester substrate.

Clean Version of Claim Amendments

20. Process according to claim 17, wherein the composition is dissolved in an appropriate solvent system.

21. Process according to claim 17, wherein the composition is applied to provide a coating having dry weight in the range from 1.5 g/m2 to 3.0 g/m2.

22. Process according to claim 17, wherein the composition is applied to provide a coating on a textured and anodized aluminum substrate or on a polyester substrate.

Atty. Docket No.
33764R003

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Andre Luiz Arias, et al.

International PCT Application No.: PCT/BR99/00079

International Filing Date: 21 September 1999

US Serial No.: To Be Assigned — Group Art Unit: To Be Assigned

Filed: : Herewith (March 21, 2001) — Examiner: To Be Assigned

For : RADIATION SENSITIVE COATING COMPOSITION USEFUL FOR LITHOGRAPHIC PRINTING PLATES AND THE LIKE

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to or concurrent with calculation of the filing fees, please amend this application as follows.

IN THE CLAIMS

Applicants have attached to this Preliminary Amendment documents entitled "Amended Claims" and "'Marked-up' Copy of the Previous Claims". Please replace present claims 8, 9, 13, 15, 16, 17, 19, 20, 21 and 22 in this application with amended claims 8, 9, 13, 15, 16, 17, 19, 20, 21 and 22 shown in the document entitled "Amended Claims".

REMARKS

Entry and consideration of this Preliminary Amendment courteously are solicited prior to or concurrent with calculation of the filing fees with respect to the claim set presented with the Preliminary Examination Report being filed herewith.

Atty. Docket No.:
33764R003

Examination on the merits is awaited.

Respectfully submitted,

SMITH, GAMBRELL & RUSSELL, LLP

By:_____

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Telephone: (202) 659-2811
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March 21, 2001

Amended Claims

Amended Claims

8. A composition according to claim 6, wherein the anion, which determines the released free acid, includes chloride, bisulfate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, methane sulfonate and mesitylene sulfonate.

9. A composition according to claim 6, wherein the onium salt is diphenyliodonium hexafluorophosphate or 3-methoxy-4-diazodiphenylamine hexafluorophosphate.

13. A composition according to claim 1, wherein it comprises the use as in the write-the-background mode and as in the write-the-image mode:

1. **Write-the-background mode**

dual polymer binder,	
* polyphenolic	50 - 95%
* polyhydric	5.0 - 40%
infrared absorber	0.1 - 12%
acid generator	0.1 - 12%
stabilizing acid (optional)	0.1 - 10%

2. **Write-the-image mode**

Dual polymer binder,	
*polyphenolic	5 - 95%
* polyhydric	10 - 90%
infrared absorber	0.1% - 12%
acid generator	0.1% - 15%
stabilizing acid (optional)	0.1 - 10%

15. The use of a radiation sensitive composition as defined in claim 1, wherein it is used for coating substrates, particularly lithographic printing plates and in color proofing films or photoresist applications.

16. A lithographic printing plate, wherein it comprises a coating prepared from a composition according to claim 1.

17. A process for printing or image development, wherein said process comprises the use of a composition as defined in claim 1, for forming a coating upon a support and developing an image from the support coated with said composition.

19. Process according to claim 17, wherein it is applied to a lithographic printing plate and said plate is subjected to cure after development.

20. Process according to claim 1, wherein the composition is dissolved in an appropriate solvent system.

21. Process according to claim 1, wherein the composition is applied to provide a coating having a dry weight in the range from 1.5 g/m2 to 3.0 g/m2.

22. Process according to claim 1, wherein the composition is applied to provide a coating on a textured and anodized aluminum substrate or on a polyester substrate.

"Marked-Up" Copy of the Previous Claims

8. A composition according to claim 6 [or 7], wherein the anion, which determines the released free acid, includes chloride, bisulfate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, methane sulfonate and mesitylene sulfonate.

9. A composition according to claim 6 [or 7], wherein the onium salt is diphenyliodonium hexafluorophosphate or 3-methoxy-4-diazodiphenylamine hexafluorophosphate.

13. A composition according to [any of the preceding claims] claim 1, wherein it comprises the use as in the write-the-background mode and as in the write-the-image mode:

1. **Write-the-background mode**

dual polymer binder,	
* polyphenolic	50 - 95%
* polyhydric	5.0 - 40%
infrared absorber	0.1 - 12%
acid generator	0.1 - 12%
stabilizing acid (optional)	0.1 - 10%

2. **Write-the-image mode**

Dual polymer binder,	
*polyphenolic	5 - 95%
* polyhydric	10 - 90%
infrared absorber	0.1% - 12%
acid generator	0.1% - 15%
stabilizing acid (optional)	0.1 - 10%

15. The use of a radiation sensitive composition as defined in [any of the claims 1 to 14] claim 1, wherein it is used for coating substrates, particularly lithographic printing plates and in color proofing films or photoresist applications.

16. A lithographic printing plate, wherein it comprises a coating prepared from a composition according to [any claims 1 - 14] claim 1.

17. A process for printing or image development, wherein said process comprises the use of a composition as defined in [any of claims 1 - 14] claim 1, for forming a coating upon a support and developing an image from the support coated with said composition.

19. Process according to claim 17 [or 18], wherein it is applied to a lithographic printing plate and said plate is subjected to cure after development.

20. Process according to [any of the preceding claims] claim 1, wherein the composition is dissolved in an appropriate solvent system.

21. Process according to [any of the preceding claims] claim 1, wherein the composition is applied to provide a coating having a dry weight in the range from 1.5 g/m2 to 3.0 g/m2.

22. Process according to [any of the preceding claims] claim 1, wherein the composition is applied to provide a coating on a textured and anodized aluminum substrate or on a polyester substrate.

Title: "RADIATION SENSITIVE COATING COMPOSITION USEFUL FOR LITHOGRAPHIC PRINTING PLATES AND THE LIKE"

Field of the Invention

The invention relates to new radiation sensitive compositions, suitable for coating substrates, particularly lithographic printing plates, color proofing films or photoresist.

Background of the Art

Compositions used in heat sensitive lithographic printing plates are well known in the art.

Compositions for coating lithographic plates comprising a phenolic resin-developer complex and a compound forming a complex with the phenolic resin were taught in the art.

It is an object of the present invention to provide new radiation sensitive compositions, specially suitable for use on printing plates, color proofing films and photoresist.

It is another object of the present invention the products manufactured with the use of radiation sensitive compositions of the present invention.

It is another object of the present invention to provide a process for manufacturing offset lithographic printing plates, color proofing films and related products using the new compositions of the present invention.

It still refers to said compositions for preparing the products mentioned herein.

Summary of the Invention

The novel radiation sensitive composition is comprised of: 1) a dual polymer binder system, 2) an infrared absorbing compound, 3) an acid generating compound and, optionally, 4) a stabilizing acid.

Detailed Description of the Invention

The radiation sensitive compositions of the present invention for coating substrates comprise 1) a dual polymer binder system, 2) an infrared absorbing compound, 3) an acid generating compound, and, optionally, 4) a stabilizing acid.

1. Dual polymer binder system

The first polymer of the binder system is a condensation product of phenol, o-chlorophenol, o-, m- or p-cresol, p-hydroxy benzoic acid, 2-naphthol or other monohydroxy aromatic monomer with an aldehyde such as formaldehyde, acetaldehyde, fural, benzaldehyde, or any other aliphatic or aromatic aldehyde. This polymer is preferred to have a molecular weight in the range from 2,000 to 80,000, more preferably in the range from 4,000 to 40,000, and most preferably in the range from 7,000 to 20,000.

The second polymer of the system is the condensation product of catechol, resorcinol, hydroquinone, bisphenol A, bisphenol B, trihydroxybenzene, or other di- or polyhydroxy aromatic compound, and methylolated analogs thereof, with an aldehyde such as formaldehyde, acetaldehyde, fural, benzaldehyde, or any other aliphatic or aromatic aldehyde. This polymer is preferred to have a molecular weight in the range from 150 to 15,000, more preferably in the range from 400 to 10,000, and most preferably in the range from 600 to 4,000.

2. Infrared absorbing compound

The infrared absorber may be either a dye or insoluble material such as carbon black. Preferred dyes are those derived from classes that include, but not limited to pyridyl, quinolinyl, benzoxazolyl, thiazolyl, benzothiazolyl, oxazolyl and selenazolyl. Carbon black is useful in that it is a panchromatic absorber and functions well with energy sources in the full spectrum of infrared useful for the application of imaging coating films, and is inexpensive and readily available. This region begins in the near infrared (NIR) at 750 nm and goes up to 1200 nm. The disadvantage of carbon black is the inability to participate in image differentiation. Dyes, in comparison, are just beginning to arise as commercial products, and are very expensive. They must be carefully selected so that the absorption λmax (lambda maximum) is closely matched with the output wavelength of the laser used on the image setter. Dyes will advantageously enhance the differentiation between the image and non-image areas created when the laser images in the medium being employed.

3. Acid generating compound

The acid generating compound is advantageously selected from the various onium salt classes. These include, but are not limited to sulfonium, sulfoxonium, arsonium, iodonium, diazonium, bromonium, selenonium and phosphonium. Generally, any compound capable of liberating a strong inorganic acid upon the onium salt being decomposed by heat, will be functional in this composition. The anion, which determines the released free acid, includes, but is not limited to chloride, bisulfate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, methane sulfonate and mesitylene sulfonate. More specific examples include diphenyliodonium hexafluorophosphate, 3-methoxy-4-diazodiphenylamine hexafluorophosphate.

4. Stabilizing acid

The optional stabilizing acid compound is added to enhance the shelf life of the coated medium prior to being imaged. Carboxylic acids are preferred. More preferred are aromatic acids. Examples of such acids are benzoic acid and substitutes thereof and naphthoic acid and substitutes thereof.

The coating composition is dissolved in a suitable solvent(s). Examples of such solvents include, but are not limited to: 1-methoxy-2-ethanol, 1-methoxy-2-propanol, acetone, methyl ethyl ketone, diisobutyl ketone, methyl isobutyl ketone, n-propanol, isopropanol, tetrahydrofuran, butyrolactone, and methyl lactate.

The coating components may be added to various solid levels based upon the technique used to apply the coating to the substrate being coated. Therefore, the ratios of components may be the same, but the percentages could differ. The percentage ranges inherent to the amounts of each of the coating components will therefore be described herein as a percentage of the total solids.

This composition may be applied to different substrates for different purposes. Essentially, it can be used for manufacturing lithographic printing plates and in color proofing films or photoresist.

If applied to a textured and anodized aluminum surface, the coated product may be used as a lithographic or offset printing plate. If the composition is applied to a support, e.g. a polyester support, it may be advantageously used as a color proofing film.

When used for the manufacture of a printing plate, the composition is primarily sensitive to energy in the infrared (IR) region. There is essentially no sensitivity in the visible region of the spectrum. However, depending upon the specific infrared absorber selected, the composition may be made to respond in the ultraviolet region (UV). This would afford the additional advantage of being both IR and UV sensitive.

As to the processing of printing plates, the printing plates are preferably placed on an image setter for radiation and imaging. Such image setters may output at any wavelength. Presently there are two common wavelengths used. An array of laser diodes emitting at 830 nm is commercially available. Such a device is manufactured and sold by Creo, Vancouver, Canada. A YAG laser outputting at 1064 nm, manufactured and sold by Gerber, a division of Barco, Gent, Belgium, is also in the market. Each wavelength has its own advantages and disadvantages. Both, however, are capable of producing acceptcapable images according to the specific manufacturing mode or way used. Digitized information is then used for modulating the laser output.

The energy is directed to the plate surface where an energy transfer mechanism occurs. In the coating, the laser dye or infrared absorbing medium absorbs the energy emitted by the laser and releases that energy as heat. Such heat in turn causes the degradation of the acid generator held within the coating, which results in the release of a strong acid. Such acid in turn causes a reaction to occur between the polymers. The reaction may be a photo-hardening reaction that makes this a "write-the-image" approach. In such a process, the area struck with energy becomes the image while the remainder of the coating is removed in the developing process. On the other hand, if the reaction causes a photosolubilization, it is a so-called "write-the-background" approach. Here the portion of the coating struck with energy is removed in the developing process, and the unaffected area becomes the image.

Depending upon the wavelength used for imaging, and the specific composition, the energy provided by the laser may be sufficient to adequately initiate the reaction and take it to completion. In instances when the energy is not sufficient, additional energy is required, which is typically applied in the form of a pre-heating step. Pre-heating may be accomplished by running the plate through an oven after being imaged and prior to being developed. The temperature is typically in the range from 80° to 150°C. A most common temperature is about 110°C. The time required at said temperature is usually between 30 and 200 seconds, more commonly about 1 minute.

By adjusting the formulation, it is also possible to use the heating step to cause the image to reverse. For instance, a plate imaged in the "write-the-background" mode would be expected to have the coating removed from the background when processed, as would be expected from the processing of a positive plate. When heated, it is possible to cause the image to reverse, such that the area exposed to laser radiation and now heated becomes the image. Therefore, the portion of the coating exposed to laser radiation becomes the image when heated, and that portion of the coating not exposed to laser radiation becomes the soluble upon development. The ability to cause this reversal is determined by the ratio of the two polymers used.

All coating compositions described herein are developed using a developer composition, which is usually completely aqueous and has a high pH. Developers typically used for positive plates are most useful. The developer takes advantage of the differentiation created with the exposure to remove the background coating and allow the image to remain. At this point the image is capable of some performance on printing machine, particularly if the required number of impressions is low. For performance enhancing, the coating may be baked. The baking step completes the cross-linking of the polymers and results in an image capable of providing several thousand times more images than without baking. The temperature range is from about 180° to 260°C. Most commonly 230°C is used. The time in this step usually ranges from 1 to 10 minutes. Most commonly 4 - 5 minutes is used. Baking is usually performed within a conveyor oven such as those sold by Wisconsin Oven.

Typical compositions within the scope of the invention are as follows:

1. **Write-the-background mode**

dual polymer binder,

* polyphenolic	50 - 95%
* polyhydric	5.0 - 40%
infrared absorber	0.1 - 12%
acid generator	0.1 - 12%
stabilizing acid (optional)	0.1 - 10%

2. **Write-the-image mode**

dual polymer binder,	
* polyphenolic	5 - 95%
* polyhydric	10 - 90%
infrared absorber	0.1 - 12%
acid generator	0.1 - 15%
stabilizing acid (optional)	0.1 - 10%

More particular compositions in the scope of the present invention include:

1A. **Write-the-background mode**

	COMPOSITION A	COMPOSITION B
dual polymer binder,		
* polyphenolic	50 - 90%	60 - 95%
* polyhydric	5 - 35%	10 - 40%
infrared absorber	0.5 - 12%	0.1 - 10%
acid generator	0.5 - 12%	0.1 - 10%
stabilizing acid	0.1 - 10%	0.1 - 10%

2A. **Write-the-image mode**

	COMPOSITION A'	COMPOSITION B'
dual polymer binder,		
* polyphenolic	5 - 40%	60 - 95%
* polyhydric	40 - 90%	10 - 40%
infrared absorber	0.5 - 12%	0.1 - 10%
acid generator	1.0 - 15%	0.1 - 10%

stabilizing acid	0.1 - 10%

For the "write-the-background" approach, according to a more specific and particular embodiment of the invention, the polyphenolic polymer (first polymer) is preferably used in the range from about 50% to about 90%, more preferably from about 55% to about 80% and most preferably from about 60% to about 75%. The polyhydric polymer (second polymer) is preferably used in the range from about 5% to about 35%, more preferably from about 8% to about 25%, and most preferably from about 10% to about 18%. The infrared absorbing compound is preferably used in the range from about 0.5% to about 12%, more preferably from about 1% to about 10%, and most preferably from about 2% to about 7%. The photoacid generating compound is preferably used in the range from about 0.5% to about 12%, more preferably from about 1% to about 10%, and most preferably from about 2% to about 7%. The stabilizing acid (optional component) is preferably used in the range from about 0.1% to about 10%, more preferably from about 0.5% to about 7%, and most preferably from about 1% to about 5%.

For the "write-the-image" approach, according to a more specific and particular embodiment of the invention, the polyphenolic polymer (first polymer) is preferably used in the range from about 5% to about 40%, more preferably from about 10% to about 35%, and most preferably from about 15% to about 30%. The polyhydric polymer (second polymer) is preferably used in the range from about 40% to about 90%, more preferably from about 45% to about 80%, and most preferably from about 50% to about 70%. The infrared absorbing compound is preferably used in the range from about 0.5% to about 12%, more preferably from about 1% to about 10%, and most preferably from about 2% to about 7%. The photoacid generating compound is preferably used in the range from about 1% to about 15%, more preferably from about 2% to about 12%, and most preferably from about 4% to about 10%. The stabilizing acid compound (optional component) is preferably used in the range from about 0.1% to about 10%, more preferably from about 0.5% to about 7%, and most preferably from about 1% to about 5%.

The coating components are dissolved in the desired solvent system. The coating solution is applied to the substrate of choice. The coating is applied so as to have a dry coating weight in the range from about 1.5 g/m^2 to about 3.0 g/m^2, more preferably from about 1.8 g/m^2 to about 2.7 g/m^2, and most preferably from about 2.0 g/m^2 to about 2.5 g/m^2. The coating is dried under conditions that will effectively remove all solvent, but no so ag-

gressive as to cause some degradation of the acid generator or reaction of the polymers with themselves or with each other.

The following non-limiting examples illustrate the invention:

Example 1

A coating solution was prepared by dissolving 6.6 g of Bakelite 744 (a novolak resin sold by Bakelite), 13.4 g of HRJ 11482 resin (a polyhydric resin sold by Schenectady), 1.0 g of laser dye 830A (sold by ADS, Montreal, Canada), 1.6 g of diphenyliodonium hexafluorophosphate, and 0.4 g of naphthoic acid in 58 g of 1-methoxy-2-propanol and 19 g of methyl ethyl ketone. An aluminum substrate which has been degreased, electrochemically grained, anodized, and made hydrophilic with a polyvinyl phosphonic acid treatment, as is well known to one skilled in the art, was coated with the above composition. When properly dried, the plate was placed on a Creo Trendsetter image setter, imaging is done in the "write-the-image" mode using 200 mJ/cm^2 of energy at 830 nm. The plate was developed through a processing machine which was charged with IBF-PD positive developer. The developed plate was observed to have a very strong positive image with good resolution. Based upon an UGRA scale, the microlines were 8/10 and the halftone dot resolution was 2 - 98. Under standard printing conditions, the plate was observed to print about 20,000 good impressions.

Example 2

Another plate was prepared as described in example 1 except that after imaging, and prior to development, the plate was given a heat treatment for one minute at 110°C. The plate was similarly developed in a positive developer. Again a positive image was observed. The image was observed to be more intense. The microline resolution was 4/6 and the halftone dot resolution was 0.5 - 99.5. Under standard printing conditions, the plate was observed to print about 70,000 good impressions.

Example 3

Another plate was prepared exactly as described in example 2. After development, the plate was baked for five minutes at 230°C. Under standard printing conditions, the plate was observed to print about 20,000 good impressions.

Example 4

A coating solution was prepared by dissolving 13.6 g of Bakelite 744 (a novolak resin sold by Bakelite), 3.0 g of HRJ 11482 resin (a polyhydric resin sold by Schenectady), 2.4 g of carbon black, 0.6 g of 3-methoxy-4-diazodiphenylamine hexafluorophosphate, and 0.4 g of benzoic acid in 81.6 g of 1-methoxy-2-propanol and 20 g of methyl ethyl ketone. An aluminum substrate which has been degreased, electrochemically grained, anodized, and made hydrophilic with a polyvinyl phosphonic acid treatment, as is well known to one skilled in the art, is coated with the above composition. When properly dried, the plate was placed on a Creo Trendsetter image setter. Imaging was done in the "write-the-background" mode using 200 mJ/cm^2 of energy at 830 nm. The plate is developed through a processing machine which was charged with IBF-PD positive developer. The developed plate was observed to have a reverse image. The portion of the coating which was imaged is now the background. The image resolution was however very good. Based upon an UGRA scale, the microlines were 10/8 and the halftone dot resolution was 2 - 98. Under standard printing conditions, the plate was observed to print about 25,000 good impressions.

Example 5

Another plate was prepared as described in example 4 except that after imaging, and prior to development, the plate was given a heat treatment for one minute at 110°C. The plate was similarly developed in a positive developer. This time a positive image was observed. Heating has caused the image to reverse. The image was observed to be more intense and have better resolution than the reversed counterpart. The microline resolution was 4/6 and the halftone dot resolution was 0.5 - 99. Under standard printing conditions, the plate was observed to print about 95,000 good impressions.

Example 6

Another plate was prepared exactly as described in example 5. After development, the plate was baked for five minutes at 230°C. Under standard printing conditions, the plate was observed to print about 3,400,000 good impressions.

Example 7

A coating solution was prepared by dissolving 17 g of Bakelite 744 (a novolak resin sold by Bakelite), 3.8 g of HRJ 11482 resin (a polyhydric resin sold by Schenectady), 1.0 g of carbon black, and 0.8 g of 3-methoxy-4-diazo-2-diphenylamine hexafluorophosphate, and 58.6 g of 1-methoxy-2-propanol and 19.2 g of methyl ethyl ketone. An aluminum

substrate which has been degreased, electrochemically grained, anodized, and made hydrophilic with a polyvinyl phosphonic acid treatment, as is well known to one skilled in the art, was coated with the above composition. When properly dried, the plate was placed on a Crescent 30 image setter and imaging was done in the "write-the-image" mode using 275 mJ/cm^2 of energy at 1064 nm. The plate was developed through a processing machine which was charged with IBF-PD positive developer. The developed plate was observed to have a very strong positive image with good resolution. Based upon an UGRA scale, the microlines were 6/10 and the halftone dot resolution was 1 - 98. Under standard printing conditions, the plate was observed to print about 23,000 good impressions.

Example 8

Another plate was prepared as described in example 7 except that after imaging, and prior to development, the plate was given a heat treatment for one minute at 110°C. The plate was similarly developed in a positive developer. Again a positive image was observed. The image was observed to be more intense. The microline resolution was 4/6 and the halftone dot resolution was 0.5 - 99.5. Under standard printing conditions, the plate was observed to print about 85,000 good impressions.

Example 9

Another plate was prepared exactly as described in example 8. After development, the plate was baked for five minutes at 230°C. Under standard printing conditions, the plate was observed to print about 2,350,000 good impressions.

Example 10

A coating solution was prepared by dissolving 15.8 g of Bakelite 744 (a novolak resin sold by Bakelite), 5.0 g of HRJ 11482 resin (a polyhydric resin sold by Schenectady), 1.6 g of carbon black, 0.2 g of laser dye 1060 A (manufactured and sold by ADS), and 0.6 g of diphenyliodonium hexafluorophosphate, in 81.6 g of 1-methoxy-2-propanol and 20 g of methyl ethyl ketone. An aluminum substrate which has been degreased, electrochemically grained, anodized, and made hydrophilic with a polyvinyl phosphonic acid treatment, as is well known to one skilled in the art, was coated with the above composition. When properly dried, the plate was placed on a Crescent 30 image setter. Imaging was done in the "write-the-background" mode using 275 mJ/cm^2 of energy at 1064 nm. The plate was developed through a processing machine which was charged with IBF-PD positive developer.

The developed plate was observed to have a reverse image. The portion of the coating which was imaged is now the background. The image resolution was however very good. Based upon an UGRA scale, the microlines were 10/6 and the halftone dot resolution was 2 - 98. Under standard printing conditions, the plate was observed to print about 20,000 good impressions.

Example 11

Another plate was prepared as described in example 10 except that after imaging, and prior to development, the plate was given a heat treatment for one minute at 110°C. The plate was similarly developed in a positive developer. This time a positive image was observed. Heating has caused the image to reverse. The image was observed to be more intense and have better resolution than the reversed counterpart. The microline resolution was 4/8 and the halftone dot resolution was 1 - 99. Under standard printing conditions, the plate was observed to print about 80,000 good impressions.

Example 12

Another plate was prepared exactly as described in example 11. After development, the plate was baked for five minutes at 230°C. Under standard printing conditions, the plate was observed to print about 2,800,000 good impressions.

Claims

1. A radiation sensitive composition, wherein the composition comprises: 1) a dual polymer binder system, 2) an infrared absorbing compound, 3) an acid generating compound and, optionally, 4) a stabilizing acid.

2. A composition according to claim 1, wherein the dual polymer binder system comprises a first polymer comprised of a condensation product of phenol, o-chlorophenol, o-, m- or p-cresol, p-hydroxy benzoic acid, 2-naphthol or other monohydroxy aromatic monomer with an aldehyde such as formaldehyde, acetaldehyde, fural, benzaldehyde, or any other aliphatic or aromatic aldehyde;

and a second polymer comprised of the condensation product of catechol, resorcinol, hydroquinone, bisphenol A, bisphenol B, trihydroxybenzene, or other di- or polyhydroxy aromatic compound, and methylolated analogs thereof, with an aldehyde such as formaldehyde, acetaldehyde, fural, benzaldehyde, or any other aliphatic or aromatic aldehyde.

3. A composition according to claim 1, wherein the first polymer has a molecular weight in the range from 2,000 to 80,000, more preferably in the range from 4,000 to 40,000, and most preferably in the range from 7,000 to 20,000; and the second polymer has a molecular weight in the range from 150 to 15,000, more preferably in the range from 400 to 10,000, and most preferably in the range from 600 to 4,000.

4. A composition according to claim 1, wherein the infrared absorbing compound is a dye or insoluble material such as carbon black.

5. A composition according to claim 1, wherein the infrared absorbing compound is preferably comprised of dyes derived form classes including pyridyl, quinolinyl, benzoxazolyl, thiazolyl, benzothiazolyl, oxazolyl and selenazolyl.

6. A composition according to claim 5, wherein the acid generating compound is an onium salt.

7. A composition according to claim 6, wherein the onium salt comprises sulfonium, sulfoxonium, arsonium, iodonium, diazonium, bromonium, selenonium and phosphonium.

8. A composition according to claim 6 or 7, wherein the anion, which determines the released free acid, includes chloride, bisulfate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, methane sulfonate and mesitylene sulfonate.

9. A composition according to claim 6 or 7, wherein the onium salt is diphenyliodonium hexafluorophosphate or 3-methoxy-4-diazodiphenylamine hexafluorophosphate.

10. A composition according to claim 1, wherein the stabilizing acid is a carboxylic acid.

11. A composition according to claim 10, wherein the stabilizing acid is an aromatic carboxylic acid.

12. A composition according to claim 11, wherein the stabilizing acid is a benzoic acid or a substitute thereof or a naphthoic acid or a substitute thereof.

13. A composition according to any of the preceding claims, wherein it comprises the use as in the write-the-background mode and as in the write-the-image mode:

1. **Write-the-background mode**

dual polymer binder,

* polyphenolic	50 - 95%
* polyhydric	5.0 - 40%
infrared absorber	0.1 - 12%
acid generator	0.1 - 12%
stabilizing acid (optional)	0.1 - 10%

2. **Write-the-image mode**

dual polymer binder,

* polyphenolic	5 - 95%

* polyhydric	10 - 90%
infrared absorber	0.1 - 12%
acid generator	0.1 - 15%
stabilizing acid (optional)	0.1 - 10%

14. A composition according to claim 13, wherein it comprises the use as in the write-the-background mode and as in the write-the-image mode:

1A. **Write-the-background mode**

	COMPOSITION A	COMPOSITION B
dual polymer binder,		
* polyphenolic	50 - 90%	60 - 95%
* polyhydric	5 - 35%	10 - 40%
infrared absorber	0.5 - 12%	0.1 - 10%
acid generator	0.5 - 12%	0.1 - 10%
stabilizing acid	0.1 - 10%	0.1 - 10%

2A. **Write-the-image mode**

	COMPOSITION A'	COMPOSITION B'
dual polymer binder,		
* polyphenolic	5 - 40%	60 - 95%
* polyhydric	40 - 90%	10 - 40%
infrared absorber	0.5 - 12%	0.1 - 10%
acid generator	1.0 - 15%	0.1 - 10%
stabilizing acid	0.1 - 10%	0.1 - 10%

15. The use of a radiation sensitive composition as defined in any of the

claims 1 to 14, wherein it is used for coating substrates, particularly lithographic printing plates and in color proofing films or photoresist applications.

16. A lithographic printing plate, wherein it comprises a coating prepared from a composition according to any claims 1 - 14.

17. A process for printing or image development, wherein said process comprises the use of a composition as defined in any of claims 1 - 14, for forming a coating upon a support and developing an image from the support coated with said composition.

18. A process according to claim 17, wherein it is applied to a lithographic printing plate and said plate is subjected to a heat treatment after imaging and prior to development.

19. Process according to claim 17 or 18, wherein it is applied to a lithographic printing plate and said plate is subjected to cure after development.

20. Process according to any of the preceding claims, wherein the composition is dissolved in an appropriate solvent system.

21. Process according to any of the preceding claims, wherein the composition is applied to provide a coating having a dry weight in the range from 1.5 g/m2 to 3.0 g/m2.

22. Process according to any of the preceding claims, wherein the composition is applied to provide a coating on a textured and anodized aluminum substrate or on a polyester substrate.

Abstract

The invention relates to a composition, which is primarily energy sensitive in the near infrared and infrared region, and which comprises a dual polymer system, an infrared absorbing material that absorbs at the desired wavelength, an acid generating compound, and, optionally, an acid stabilizing compound. The composition may be applied to the proper substrate and is useful to provide offset lithographic printing plates, color proofing film or photoresist.

#5

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Declaration and Power of Attorney
United States Patent Application

As a below named inventor, I hereby declare that:
My residence, post office address and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor *(if only one name is listed below)* or an original, first and joint inventor *(if plural names are listed below)* of the subject matter which is claimed and for which a patent is sought on the invention entitled

"Radiation sensitive coating composition useful for lithographic printing plates and the like", the specification of which

(check one)
- ☒ is attached hereto.
- ☐ was filed on March 21, 2001 as U.S. Application Serial No. 09/787,667 and *(if applicable)* was amended on _____.
- ☒ was filed as PCT International Application No. PCT/BR99/00079 on September 21,1999 and *(if applicable)* was amended under PCT Article 19 on _____.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign and PCT application(s) for patent or inventor's certificate listed in this Declaration and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Foreign/PCT Application No.	Country	Filing Date	Priority Claimed? (yes/no)
PI 9803946-6	BR	September 21,1998	yes
PI 9901906-0	BR	April 19, 1999	yes
PCT/BR99/00079	PCT	September 21, 1999	yes

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) and PCT International Application(s) listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Application No.	Filing Date	*Status (patented/pending/abandoned?)*
PCT/BR99/00079	September 21,1999	

I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Joseph A. DeGrandi (17446), Robert G. Weilacher (20531), Richard G. Young (20628), Michael A. Maluch (32263), Bernard A. Meany (22891), Helen M. McCarthy (32513), Dennis C. Rodgers (32736), William F. Ravchinsk (34791), G. Byron Slover (34737), Thomas L. Evans (35805), Maurice U. Calm (30454), Robert Jones Worrall (37969), and William J. Bundren (31712).

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

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BDWY 994 *(Supply similar information and signature for third and subsequent joint inventors.)*

Supplemental Sheet for Declaration and Power of Attorney

(Please use for supplying information and signatures of third and subsequent joint inventors.)

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